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# Source Measurement

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16. ABSTRACT The paper describes tests of four woodstove operating parameters at two levels each: burn rate, wood moisture, wood load, and wood type. A half-factorial experimental test design allowed statistical evaluation of the effects of each parameter on measured emissions of polycyclic aromatic hydrocarbons (PAHs), particulates, total hydrocarbons (THCs), CO, elements, and C1-C7 hydrocarbons. The control of burn rate and wood moisture content were the most statistically significant parameters affecting organic emissions. Elemental emissions were most significantly affected by burn rate and wood type. Increased burn rates lowered CO, particulate, THC, C1-C7, and total PAH emissions. However, emission rates of seven individual PAHs increased. Elemental emissions of Ca, K, Mn, S, and Zn increased. Reduced wood moisture increased particulate emission factors, and decreased total PAH emissions. Naphthalene, acenaphthylene, fluorene, and anthracene concentrations were reduced. The pyrene emissions factor decreased. A change from pine to oak decreased emissions of acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, and Mn, while increasing K. Increased wood load increased particulate emission rates. Overall, significant changes, even reductions in total organic emissions, can be made just by the way a woodstove is operated.

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| Stoves | Stationary Sources | 13A 07B |
| Wood | Woodstoves | 11L |
| Hydrocarbons | Particulate | 07C |
| Carbon Monoxide | | 14G |
| Elements | | 11G |
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Integrated Air Cancer Project, Source Measurement

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## Abstract

Four woodstove operating parameters were tested at two levels each: burn rate, wood moisture, wood load, and wood type. A half-factorial experimental test design allowed statistical evaluation of the effects of each parameter on measured emissions of polycyclic aromatic hydrocarbons (PAHs), particulates, total hydrocarbons (THCs), carbon monoxide (CO), elements, and $C_1$-$C_7$ hydrocarbons. The control of burn rate and moisture content of wood were the most statistically significant parameters affecting organic emissions. Elemental emissions were most significantly affected by burn rate and wood type. Increased burn rates lowered CO, particulate, THC, $C_1$-$C_7$, and total PAH emissions. However, emission rates of the individual PAHs--naphthalene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene--increased. Elemental emissions of Ca, K, Mn, S, and Zn increased. Reduced wood moisture increased particulate emission factors, and decreased total PAH emissions. Naphthalene, acenaphthylene, fluorene, and anthracene concentrations were reduced. The pyrene emissions factor decreased. A change from pine to oak decreased emissions of acenaphthylene, fluorene, phenanthene, anthracene, pyrene, and Mn, while increasing K. Increased wood load increased particulate emission rates. Overall, significant changes, even reductions in total organic emissions, can be made just by the way a woodstove is operated. All tests were performed on one typical noncatalytic woodstove.

## Introduction

The use of wood for residential heating has become a widespread practice in recent years. As of the end of 1983, there were an estimated 10.6 million residential wood combustion (RWC) units in use. As referred to here, RWC units consist of freestanding woodstoves and fireplace inserts, but do not include open fireplaces. Recently there has been an increasing concern over the potential environmental health hazards related to the emissions from residential wood combustion sources as they have been implicated as major contributors to the seasonal decline of air quality in several regions[1],[2],[3]. In certain localized areas, woodsmoke has become a seasonal problem because of the accumulation of noticeably large, lingering smog-type clouds. One study in a residential neighborhood with a density of woodstoves and fireplaces of about 60 units/$km^2$ indicated that wood heating can significantly impact the ambient air quality of local areas with a concentrated use of woodstoves and fireplaces[1]. Emissions from RWC are a growing problem throughout all areas of the country where wood supplies are abundant. In fact, several areas are currently violating national ambient air quality standards (NAAQS) for particulate matter (PM) and carbon monoxide (CO) due to RWC[4]. Particulate matter is emitted at significant levels from RWC, and a large portion of PM is respirable and poses a real health hazard in areas of high woodsmoke concentration. Polycyclic aromatic hydrocarbons (PAHs) or polycyclic organic matter (POM) is indicated as the main source of mutagenic activity in woodsmoke. A recent compilation of an emission inventory for POM indicates that residential woodburning may be the largest source of POM emitted to the atmosphere[5]. Other organic emissions of interest in this study include total hydrocarbons and $C_1$-$C_7$ aliphatic hydrocarbons. Stack emissions of CO are also of great concern. A recent study has shown that significant increases in ambient CO levels in one area directly reflected stove usage. The elements Fe and K are of interest for use as woodsmoke identifiers.

During 1985, the Environmental Protection Agency's Integrated Air Cancer Project (IACP) undertook a number of tasks to develop methods for characterizing source emissions from RWC units, such as woodstoves. This paper addresses a portion of the 1985 IACP to characterize emissions from a RWC unit over a set of typical operating ranges. Specific emphasis is placed on defining the relationships between stove operating parameters and the effects of those paraemters on toxic/mutagenic emissions. Four woodstove operating parameters were tested at two levels each: burn rate, wood moisture, wood load, and wood type. A half-factorial experimental test design was used to determine statistically significant effects from changes in the operating parameters on measured emissions of CO, $CO_2$, PM, total hydrocarbons, PAHs, $C_1$-$C_7$ hydrocarbons, elements, and elemental Fe/K ratios. The direction and magnitude of main effects from changing each of the four operating variables on measured emissions are reported within 90%, 95%, and 99% confidence limits. Some main effects are reported, but are just below a 90% confidence limit.

## Experimental Methods

The following discussion is divided into four sections: first is a description of the statistical test design, second is a description of the test facility, third is a discussion of emission measurement methods used, and fourth is a discussion of analytical procedures.

## Statistical Test Design

A half-factorial experimental test design was employed to statistically evaluate the effects of four stove operating variables (burn rate, wood moisture, wood load, and fuel type) on the measured woodstove emissions. Each variable range was established according to high and low values and used in the half-factorial test matrix. Burn rate target values were previously determined to be approximately 2 kg/hr for low burn rates and 6 kg/hr for high burn rates. The experimental averages for the low and high burn rates were used for the reported range. Wood moisture contents were determined gravimetrically for cured and uncured woods. Uncured wood remained as logs, and was cut 1 day prior to testing to preserve the wood moisture content. Wood loads (kg) were determined according to the volume of the firebox. High wood loads filled the stove to capacity initially, and low wood loads filled the stove approximately half full. Wood type was defined as oak versus pine. Test variables with actual experimental values are:

| VARIABLES | HIGH<br>+ | LOW<br>- |
|---|---|---|
| Fuel | Oak | Pine |
| Moisture, % | Cured 16.9 | Uncured 33.2 |
| Load, kg | 14.0 | 8.3 |
| Burn Rate, kg/hr | 6.56 | 1.88 |

Table I illustrates the half-factorial test matrix used to evaluate these four operating variables on measured emissions.

Twelve woodstove tests were run on the same woodstove at the rate of one test per week. The first two tests were used to familiarize the test personnel with proper damper settings for desired burn rates, and to test the operation of the continuous CO, $CO_2$, and $O_2$ gas analyzers in conjunction with a Metrosonics data logger. The eight tests prescribed by the test matrix were then run. The results of test No. 3 were discounted due to sampling problems, and a repeat test was performed. The last test performed was a duplicate of test No. 2 to assess reproducibility. The statistical analysis of experimental results was performed and an analysis of variance was used to determine the significance of each variable on each measured emission[7].

The calculations of contrasts, main effects, and analyses of variance (ANOVA) tables were performed using LOTUS 1-2-3® spreadsheets. This permitted rapid insertion of results and performance of calculations. The ANOVA procedure takes any set of experimental results for the eight tests and divides the variation of the data (Sum of Squares) into variations attributable to the changed variables (fuel, moisture, load, and rate) and experimental error (error). A comparison of the sum of squares for a variable to the error sum of squares in an f-test indicates whether or not the variation of a main effect attributed to a variable (fuel, moisture, load, and rate) is statistically significant. Calculated f values are compared to tabulated f values at 99% ($\alpha = 0.1$), 95% ($\alpha = 0.05$), and 90% ($\alpha = 0.10$) confidence intervals.

## Test Facility

The stove used was a Sears Catalog No. 42G84156N free-standing noncatalytic radiant woodstove. A schematic overview of the stove and sampling system is shown in Figure 1. A hinged door on the right side houses three screw-down air dampers. The air inlet dampers are each 3 in. (7.6 cm) in diameter and form a triangle on the door. These dampers were used to control the amount of air into the stove, and thus, the burn rate. The interior of the stove is lined with firebrick and has an internal volume of 0.068 $m^3$. The stove is baffled, and the flue exit is in the rear, opposite the hinged interlocking front doors. The legs of the stove were removed, and the entire stove and flue sections were mounted on a leveled digital Detecto 5850 scale which was calibrated to 1000 lb (454 kg) just prior to this study. The flue exit from the rear of the stove is 6 in. (15.2 cm) in diameter and the flue's inside diameter is 8 in. (20.3 cm). A single-walled 6-/8-in. adaptor was used to connect the stove exit to an 8-in. (20.3 cm) inside diameter double-walled Metalbestos insulated tee. All sections of the flue from the tee upward consisted of the same type of double-walled insulated flue. From the tee, two 30-in. (76 cm) and two 9-in. (22.9 cm) vertical flue sections were mounted. Sections of 30-in. flue were then added to extend the flue out of the roof of the test facility.

A removable Modified Method 5 glass probe and two type K thermocouples were installed in the uppermost 9-in. (22.9 cm) flue section. The next segment, another 30-in. (76 cm) section of flue, held three 6 in. x 1/2-in. (15.2 cm x 1.3 cm) stainless steel probes for flue gas analyses. They were inserted approximately 8 in. (20.3 cm) above the Method 5 probe. The stainless steel probes were oriented at approximately 120 degree intervals around the flue, and each was elevated above the other by approximately 1/2-in. (1.3 cm). The probes penetrated the flue interior to approximately 3-1/2 in. (8.9 cm). Clean glass wool was placed in each probe before each test. The first probe was used to measure continuous samples for carbon monoxide, carbon dioxide, and oxygen concentrations. Instruments measuring these gas concentrations in the flue gas were connected in series. The second of the three probes was used to sample total hydrocarbon concentrations. A 1/4 in. x 1/2 in. (0.64 cm x 1.3 cm) stainless steel line was connected to a Beckman 400 FID, which was located in a hood. The line was heated with several heating tapes and was maintained at ~200 °C during sampling. The third probe initially was to be used for sampling a composite bag sample for $C_1$-$C_7$ hydrocarbon analyses. However, due to experimental problems, all $C_1$-$C_7$ hydrocarbon bag samples were taken from the bypass line of the Beckman 400 FID. The probe was removed and the bulkhead was capped for all tests.

Four Type K thermocouples were attached to the exterior of the stove to monitor the stove box temperature. The wires were connected such that the outputs were averaged in one channel into a Metrosonics 721 data logger. The two stack thermocouples were also averaged in the same manner and represented a separate channel to the data logger. Cold reference junctions were used for each temperature recorded by the data logger.

The digital output from the Detecto Scale was mounted on a panel outside the test room. The weight of wood was recorded manually as each log was loaded until the proper loading was reached. At regular intervals, the mass of

wood was manually recorded, and the burn rate (kg/hr) was calculated and monitored. Room temperature was monitored with a separate Type K thermocouple and readout which was located approximately 4 ft (1.2 m) from the stove in a 1 x 6 in. (2.54 x 15.2 cm) stainless steel pipe. Near the room temperature thermocouple, an Abbeon⊙ Certified Hygrometer was used to monitor the relative humidity (RH) in the test room. During tests, the RH and temperature of the test room were periodically recorded.

A Kurz⊙ hotwire anemometer was used periodically to record the air flow through the two opened dampers low on the stove door (the upper damper was always closed). A small section of 3 in. (7.6 cm) pipe was placed over each damper, and the hotwire was placed directly in front of the pipe for the periodic measurements. The intake air was re-checked whenever damper settings were changed or wood was added. A Taylor series 3231 Jeweled Anemometer was used to periodically measure the stack flow manually. The instrument was hand-held just above the flue outlet for 1 to 2 minutes for each measurement. This measurement was taken whenever damper settings were changed or the stove door was opened and wood was added. The stack flows for each test were then time averaged over the measured intervals.

## Emission Measurement

A Modified Method 5 (MM5) sampling train was used to collect an integrated sample of polycyclic organic matter. A schematic of the MM5 System is shown within Figure 1. The MM5 train was constructed of all glass/Teflon . Some modifications were instituted to tailor MM5 to woodstove emission sampling. The principal modifications were:

1. The sample rate was held constant; no attempt was made to sample isokinetically.
2. All samples were taken from a single point; there was no traversing.
3. No precutter cyclone was employed.
4. Sample recovery and subsequent extractions utilized both dichloromethane ($MeCl_2$) and methanol (MeOH) solvents. In all cases, the rinses and extractions were kept separate (i.e., $MeCl_2$ and MeOH probe rinses were done sequentially and placed in separate containers).
5. All recovered liquid samples were placed in amber glass jars and sealed with Teflon⊙ cap liners.
6. All recovered samples were frozen immediately, and subsequently stored at 0 °C.

Modifications 1-3 represent common practice when sampling woodstove emissions. Modification 4 was made to ensure complete sample recovery while preserving sample quality. Woodstove emissions are not completely soluble in $MeCl_2$, the preferred solvent for subsequent organic analyses. MeOH would remove all remaining residues and, although it might, itself, react with organics in the emissions, would permit a more accurate estimate of total emission. Samples recovered from MeOH washes were used only for mass determinations. Modification 5 was instituted to minimize sample contamination. Modifications 5 and 6 were employed to minimize sample degradation caused by ultraviolet radiation or heat.

Before each run, all glassware and fittings were chromic-acid washed, rinsed (with distilled deionized water, methanol, and methylene chloride), and then assembled. Glass fiber filters were acid washed with 500 cc of 5% nitric acid, rinsed with 2 liters of distilled deionized water, dried in a 110 °C oven for 24 hours, cooled in a desiccator, and then weighed on a Mettler HR51A analytical balance. The filters were also weighed after desiccating for 24 hours with the particulate sample collected, and after soxhlet extraction and desiccation. Filters, both used and unused, were stored in covered petri dishes and placed in a desiccator. The filters were not allowed to contact metal objects after pre-test preparation.

Teflon® sleeves and metal clamps were used on all tapered joints in the MM5 sample train. All other connections, including Swagelock® fittings, ball joints, O-ring/clamps, and impinger fittings were wrapped tightly with Teflon® tape and were tested leak tight. Teflon® tape was also wrapped around all petri dishes which contained used, extracted glass fiber filters.

After each test, MM5 samples were generated by rinsing the sampling system with methylene chloride, then methanol. Methylene chloride and methanol rinses were kept separate. The system was divided into two sections, heated and cooled. The heated section was from the glass probe to the heated filter bell assembly, and the cool section was from the exit of the heated filter bell assembly to the Teflon tube leading to the impingers.

Soxhlet extractions were done separately on the glass fiber filter(s) and XAD-2 resin after each test. The methylene chloride rinse from the heated portion of the MM5 system was termed "Probe wash $CH_2Cl_2$" and was added to the filter soxhlet extraction. The methylene chloride rinse from the cooled portion of the MM5 was termed "Condenser wash $CH_2Cl_2$" and was added to the XAD-2 soxhlet extraction. Furthermore, the condensate was extracted with portions of methylene chloride, proportional to the volume of condensate, at pH 2 $\pm$ 0.5 and 11 $\pm$ 0.5. This extract was then combined with the XAD-2 soxhlet extract and later concentrated with a Kuderna-Danish (K-D) evaporator. All solvent samples were stored in 500 cc wide-mouth amber bottles with Teflon®-lined caps. The bottles were all chromic acid washed, and rinsed with distilled deionized water, methanol, and methylene chloride prior to use. The bottles containing solvent samples were tightly capped, wrapped along the top with Parafilm , labeled, and stored in a freezer until K-D concentration. The extracted condensate, extracted XAD-2, and impinger water were also saved and stored in cleaned amber bottles.

Samples generated by the MM5 system used for organic and elemental analysis were:

1. Probe wash + filter methylene chloride extract = PWF - $CH_2Cl_2$.
2. Condenser wash + XAD-2 + condensate methlene chloride extract = CWX-$CH_2Cl_2$.
3. Probe wash methanol (gravimetric only).
4. Condenser wash methanol (gravimetric only).
5. Extracted glass fiber filter (saved for elemental analyses).

The samples listed above were analyzed for PAH, gravimetric, TCO, and spot tests (except methanol samples).

Additional data from the MM5 sample system include total volume sampled, sample gas exit temperature, and sample system pressure. CO, $CO_2$, $O_2$, ppm hydrocarbons FID, stack temperature, and stove temperature were measured continuously and recorded at two points per second on a Metrosonics data logger. The continuous gas analyzers were calibrated and checked before and after each test. $C_1$-$C_7$ bag samples were collected in appropriate sample bags from the bypass on the FID.

## Analytical Procedures

Total Hydrocarbons. Total hydrocarbons were calculated as the sum of two separate analytical procedures, gravimetric (Grav) and total chromatographable organics (TCO)[6]. The gravimetric procedure provides a measure of organics with boiling points above 300 °C, while the TCO provides a measure of organics between 100 °C and 300 °C. Total hydrocarbon analysis was performed separately on the two types of concentrated methylene chloride samples previously described.

$C_1$-$C_7$ Hydrocarbons. $C_1$-$C_7$ gas samples were collected by RTI in bag samples and were measured with GC-FIC by Industrial Environmental Analysts (IEA). A column of 0.19% picric acid on Carbopak® C was used with flame ionization detection (FID). The chromatograms were integrated and recorded with a Perkin-Elmer Sigma 10 integrator. The FID was calibrated with 5 ml of a gas standard (Supelco $C_1$-$C_6$ hydrocarbons, 100 $\pm$ 5 ppm, methane, ethane, propane, butane, pentane, and hexane) prior to 5 ml sample injection. Response factors for $C_1$-$C_6$ were calculated from the standard injection and used to calculate the sample $C_1$-$C_7$ hydrocarbon concentration. The chromatograph for the sample was divided into ranges for $C_1$, $C_2$, $C_3$, $C_4$, $C_5$, $C_6$, and $C_7$, and the response factors from the standard were applied to the sum of the peak areas in each range. The $C_7$ hydrocarbon response factor was assumed to be the same as for $C_6$ hydrocarbons. The total $C_1$-$C_7$ hydrocarbons from each test were used in the statistical analyses.

Polycyclic Aromatic Hydrocarbons. Polycyclic aromatic hydrocarbon (PAH) analyses were performed by Radian Corporation on RTI composited methylene chloride PWF, CWX samples. Capillary GC/MS was used to obtain PAH results. Composited aliquots of the methylene chloride PWF and CWX samples from each woodstove test were made and EPA Method 610 silica gel cleanup for PAH was performed. An initial total chromatographable organics (TCO) analysis on the cleaned composite samples was performed to determine if they were concentrated enough to proceed with PAH capillary GC/MS analysis. A gravimetric analysis was also performed on the cleaned samples. The TCO and GRAV analysis performed on the cleaned composite samples is used as a measure of total PAH since the Method 610 sample cleanup method was designed to isolate PAH compounds. The target compounds were:

- phenol
- naphthalene
- acenaphthylene
- acenaphthene
- fluorene
- nitronaphthalene
- phenanthrene
- phenanthrol
- pyrene
- benzo (a) anthracene
- chrysene
- benzo (b) fluoranthene
- benzo (k) fluoranthene
- benzo (a) pyrene

| | |
|---|---|
| anthracene | 3-methyl cholanthrene |
| acridine | benzo (g,h,i) perylene |
| carbozole | dibenzo (a,h) anthracene |
| fluoranthene | indeno (1,2,3 cd) pyrene |

Elemental ICAP. Elemental ICAP analyses were performed by Acurex Corporation on wood ash and MM5 glass fiber filters from each woodstove test. Additional ICAP analyses were performed on each type of wood used in the test matrix and one set of woodsmoke concentrated extract. Elements analyzed were:

| | | | |
|---|---|---|---|
| Ag | Cr | Na | Si |
| Al | Cu | Ni | Sn |
| As | Fe | P | Sr |
| Ba | Hg | Pb | Ti |
| Ca | K | S | Tl |
| Cd | Li | Sb | V |
| Co | Mg | Se | Zn |
| | Mn | | |

Continuous Measurements of Oxygen, Carbon Monoxide, Carbon Dioxide, FID Hydrocarbons, and Stove and Stack Gas Temperature. Stack gas % $CO_2$, % CO, % $O_2$, ppm hydrocarbons, and temperature, and stove temperature were continuously measured during the experimental tests. Instruments and ranges for these measurements are listed below. Outputs from the these instruments were recorded by a Metrosonics 721 data logger. The data logger measured data for six channels every 2 seconds, and then stored the high, low, and average values for each minute.

| MEASURED PARAMETER | INSTRUMENT | RANGE |
|---|---|---|
| % $CO_2$ | Horiba PIR-2000 NDIR | 0-20% |
| % CO | Horiba PIR-2000 NDIR | 0-3% |
| % $O_2$ | MSA Magnetic $O_2$ analyzer | 0-25% |
| ppm Hydrocarbon as $CH_4$ | Beckman Model 400 FID Hydrocarbon analyzer | 0-20,000 ppm |
| Stove and Stack Gas Temperature | Average of two K-type thermocouples | 10-800 °C |

Stack gas was conditioned through two condensers and a filter prior to analysis for % $CO_2$, % CO, and % $O_2$. These three analyzers were connected in series. The stack gas sample for the FID hydrocarbon analyzer was fed continuously to the analyzer though a separate heated line with a glass wool filter. This sample line was heated to approximately 200 °C.

Each instrument and data logger measurement was calibrated at zero and a span concentration prior to each test burn. The instruments and data logger were re-checked with zero and span gases at the end of each test run to check for instrument drift. Data collected with the data logger were transferred to an IBM-PC immediately after each test burn. The computer files were used with Lotus 1-2-3 spreadsheets to calculate average % $CO_2$, % CO, % $O_2$, ppm HC, stack gas temperature, and stove temperature during the Method 5 sampling period of each test burn.

## Appliance Operation

Before each test, the MM5 system was assembled and leak checked. All heated and cooled portions were brought to appropriate temperatures. The continuous gas analyzers were calibrated with zero and span gases, and readings were double-checked with the data logger. Pretest measurements of barometric pressure, relative humidity, and test room temperature were taken. Log moistures were each checked with a Delmhorst wood moisture meter. This ensured that the moisture of each log was within the proper range for the test. Once all systems were ready, an 8 in. (20.3 cm) to 12 in. (30.4 cm) pile of finely split kindling of the type of wood to be burned for the test in progress was carefully placed into the stove. A propane torch was used to ignite the pile of kindling. Paper was not used in order to preserve the integrity of the ash generated by each run. Once the kindling had burned down to a hot bed of coals, the stove weight was tared, the wood was loaded, and the weight was recorded for each split log. A total wood load was recorded, and the logs were allowed to ignite. The dampers were closed to previously determined levels, and the weight change was observed over several 5 to 10 minute intervals. Adjustments were made to the inlet air flow until the desired burn rate was attained. The burn rate was calculated and recorded manually every 5-10 minutes. A steady desired burn rate signaled the start of organic sampling from the MM5 system. Start-up organic sampling was eliminated because high emissions at that point could mask effects from the four parameters being studied. The continuous analyzers, stove, and stack gas temperatures were automatically recorded throughout the entire test. The run time recorded by the data logger was also recorded manually as were fuel weights and relevant data such as stack flow, inlet flows, relative humidity, and any other comments relevant to the run in progress. During each test, at least one recharge was performed up to the initial wood load. After the test, the total MM5 time and the weight losses during the MM5 interval were computed, and a burn rate (kg/hour) was calculated for the entire MM5 time. All other measurements taken during the MM5 sampling period were averaged over the MM5 sampling interval. The average MM5 interval was 3 hours, and the average MM5 sample volume dry gas was 2.3 $m^3$.

## Results

For the purpose of discussion, three types of emission formats are defined: concentration is mass of component per cubic meter of stack gas STP wet ($g/m^3$), emission factor is mass of component per mass of wet wood burned (g/kg), and emission rate is mass of component emitted per hour (g/hr). All reported effects are the result of the analyses of variance performed by the half-factorial statistical test design. Tables II and III list main effects with a direction and magnitude attributable to each operating parameter. These effects are referred to in the following discussion. The confidence interval (CI) attributable to the main effect (ME) is also given.

A direct result of increasing burn rate is an increase in stove temperature (+143.8 °C, 99% CI), stack gas temperature (+170.1 °C, 99% CI), and stack gas flow (+0.7 $m^3$/min, 99% CI). The control of burn rate exhibited the most statistically significant effects on the measured emissions. In Figure 2, the effects of low and high burn rate tests on CO, particulate, total hydrocarbon, and $C_1$-$C_7$ hydrocarbon emission factors are illustrated. Each emission factor

decreases when the burn rate is increased from an average of 1.88 kg/hr to an average of 6.56 kg/hr. The main effect on the carbon monoxide emission factor is a decrease of 111.5 g/kg, that occurs due to an increase in burn rate at a 90% CI. Approximately half of the amount of CO is produced from each kilogram of wood at the higher burn rates.

The particulate emission factor decreases substantially at the higher burn rates as shown in Figure 2. The main effect is a decrease of 5.6 g/kg wood burned; this effect is significant at a 99% CI. Approximately one-fourth the amount of particulate matter is produced at the higher burn rates. One interesting finding is that no statistically significant effects due to burn rate were observed on the particulate emission rate. However, increasing the initial wood load did increase the particulate emission rate by 10.1 g/hr at a 90% CI. This effect is illustrated in Figure 3. This may be explained in the following manner: at low burn rates, the concentration of particulates (see Table II) is higher, but the stack flow is lower. At higher burn rates, the concentration of particulates is lower, but the stack flow has increased. These effects may cancel each other such that wood load has the only significant effect on particulate emission rates.

The total hydrocarbon emission factor main effect decreased 47.3 g/kg with increased burn rates at a 95% CI. Figure 2 illustrates this effect. There is approximately one-fourth the amount of total hydrocarbons produced per kilogram of wood at higher burn rates. Similarly, in Figure 2, $C_1$-$C_7$ hydrocarbons decrease significantly at higher burn rates.

The total PAH emission factor also decreased with increased burn rates as shown in Figure 4. Total PAH is defined here as the sum of TCO and Gravimetric analyses[6] performed on samples which had been cleaned via the EPA Method 610 PAH analyses procedure. Although the main effect shows a decrease of 9.3 g/kg, the f-value obtained from the statistical analyses fell just below the requirement for a 90% confidence interval. This effect is still significant, but at a lower confidence interval. There is a statistically significant effect at a 90% CI on total PAH emission rates due to wood load; however, Figure 5 illustrates an increase of 22.2 g/hr of total PAH emissions rates as the initial wood load increases. This is similar to the condition described for the particulate emission rates. No statistically significant effect by the burn rate was observed on the total PAH emission rate. At low burn rates, the concentration of total PAH is higher (see Table II), but the stack gas flow is lower, and at high burn rates the total PAH concentration is lower, but the stack gas flow is higher. These effects may cancel each other, such that the amount of wood loaded directly affects the emission rate of total PAH.

While the effect of increased burn rates was to decrease total hydrocarbon (g/kg) and total PAH emission factors (mg/kg), increases in certain individual PAH emission rates (mg/hr) were observed with increased burn rates. Figure 6 illustrates the increase of naphthalene (+864.7 mg/hr), phenanthene (+136.0 mg/hr), and fluoranthene (+52.1 mg/hr) emission rates as the burn rate increased. Figure 7 illustrates the same trend for pyrene (+42.7 mg/hr), chrysene (+14.3 mg/hr), benzo(b)fluoroanthene (+15.0 mg/hr), and benzo(a)pyrene (+7.3 mg/hr). One general trend to note is that the more complex the PAHs become (naphthalene → benzo(a)pyrene), the lower the emission rate becomes.

This is evident, for the most part, in each individual test shown in Figures 6 and 7. The main effect of increased burn rates is to increase the emission rates of each of these compounds; however, the f-values generated for the changes in emission rates of these individual compounds due to changes in burn rate fell just under the requirement for a 90% confidence interval. These main effects are reported since the f-values were still much higher than values observed when there was clearly no sigificance.

As shown in Table II, a decrease in wood moisture content increased the particulate emission factor +2.22 g/kg at a 90% CI. All total PAH emissions decreased as did stack concentrations of naphthalene (-14.2 $mg/m^3$, 90% CI), acenaphthylene (-1.95 $mg/m^3$, just under 90% CI), fluorene (-0.64 $mg/m^3$), and anthracene (-0.37 $mg/m^3$). Both fluorene and anthracene main effects occurred just under the 90% CI. A change from pine to oak decreased the acenaphthylene emission factor (-24.5 mg/kg wood), fluorene emission factor (-9.46 mg/kg wood), phenanthene emission factor (-22.92 mg/kg wood), and anthracene emission factor (-4.51 mg/kg wood). Stack concentrations of acenaphthylene, fluorene, and phenanthrene also decreased from changing from pine to oak. These main effects were also just under a 90% CI.

Table III lists all elements with the main effect (ME) and confidence interval (CI) from each operating parameter. Increased burn rates increased potassium and sulfur concentrations, emission rates, and emission factors. Manganese and zinc concentrations and emission rates increased also. All effects on these elemental emissions were significant above a 90% CI, except for the zinc emission rate which occurred just under a 90% CI.

Changing from pine to oak increased the potassium concentration (+1852.9 $\mu g/m^3$, 95% CI), emission rate (+97.9 mg/hr, 90% CI), and emission factor (+20.2 mg/kg wood, 99% CI). Manganese emissions, however, decreased significantly. The manganese concentration decreased (-16.0 $\mu g/m^3$, 95% CI), as did the emission rate (-1.02 mg/hr, 90% CI) and emission factor (-0.27 mg/kg wood, 95% CI). The zinc emission factor decreased (-2.05 mg/k, wood, 90% CI). Just below a 90% CI, the sulfur emission rate increased (+5.2 mg/hr), and the zinc concentration decreased (-136.4 $\mu g/m^3$).

## Summary and Conclusions

The preceding discussion leads to the following conclusions.

A. Stove and stack gas temperatures increase significantly with an increase in burn rate.

B. Increased burn rates decrease carbon monoxide, particulate, total hydrocarbon, and $C_1$-$C_7$ hydrocarbon emission factors (g/kg).

C. Increased burn rates decrease total PAH emission factors.

D. Increased burn rates increase certain individual PAH emission rates (mg/hr).

E. Increased burn rates increase potassium and sulfur emissions ($\mu g/m^3$, g/hr, and g/kg).

F. A decrease in wood moisture content increases particulate emission factors (g/kg).

G. A decrease in wood moisture content decreases total PAH emissions ($g/m^3$, g/kg, and g/hr).

H. Changing wood from pine to oak decreases several individual PAH emission factors (g/kg).

I. Changing wood from pine to oak decreases stack concentrations of several individual PAHs.

J. Changing wood from pine to oak increases potassium emissions ($ug/m^3$, g/kg, and h/hr), but reduces manganese emissions.

K. Changing wood from pine to oak increases the sulfur emission rate (g/hr).

L. Increasing wood loads increases particulate and PAH emission rates.

M. Significant reductions in organic, particulate, and CO emissions can be achieved just by the way a woodstove is operated.

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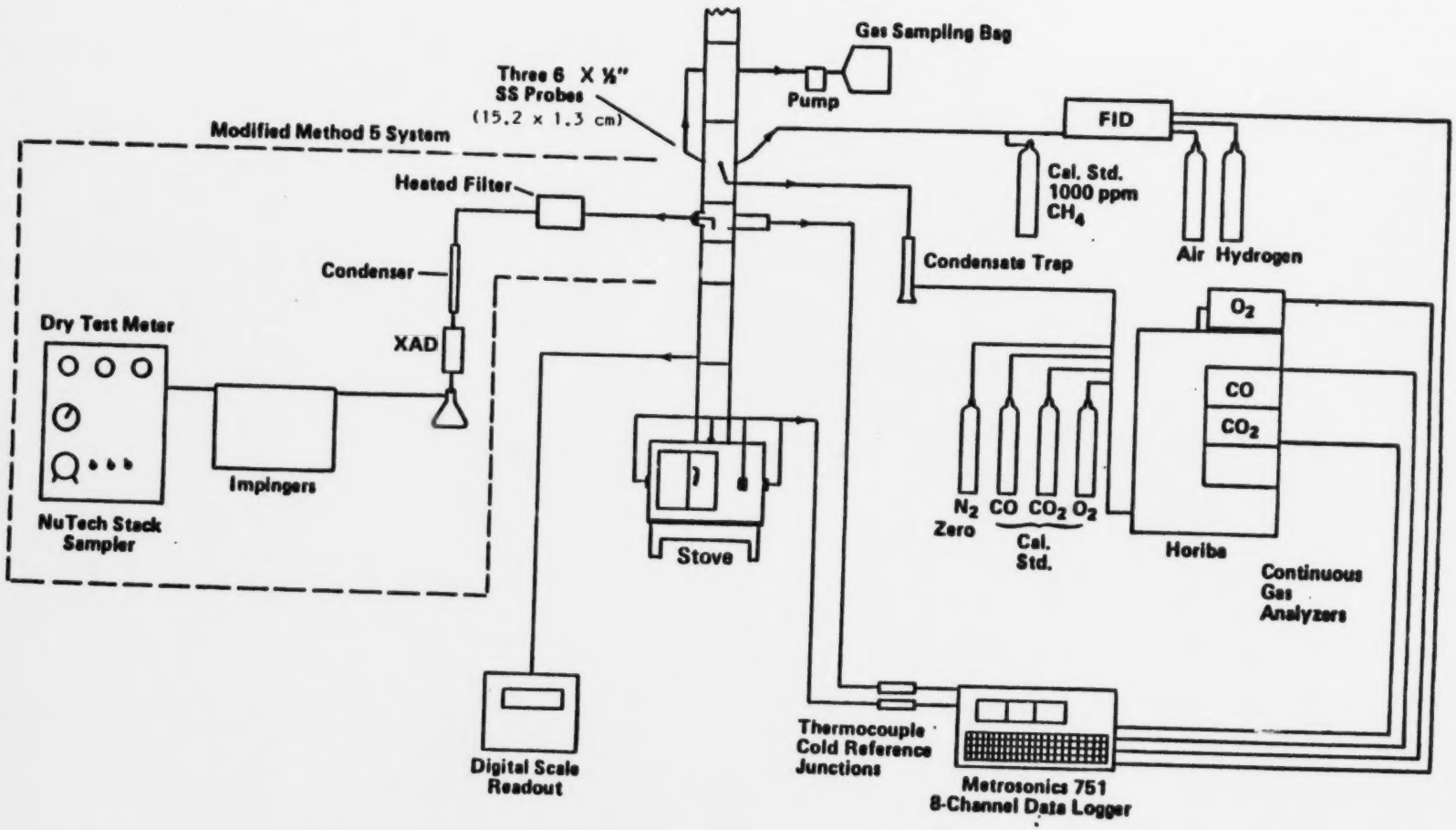


Figure 1. Woodstove and sample system overview.

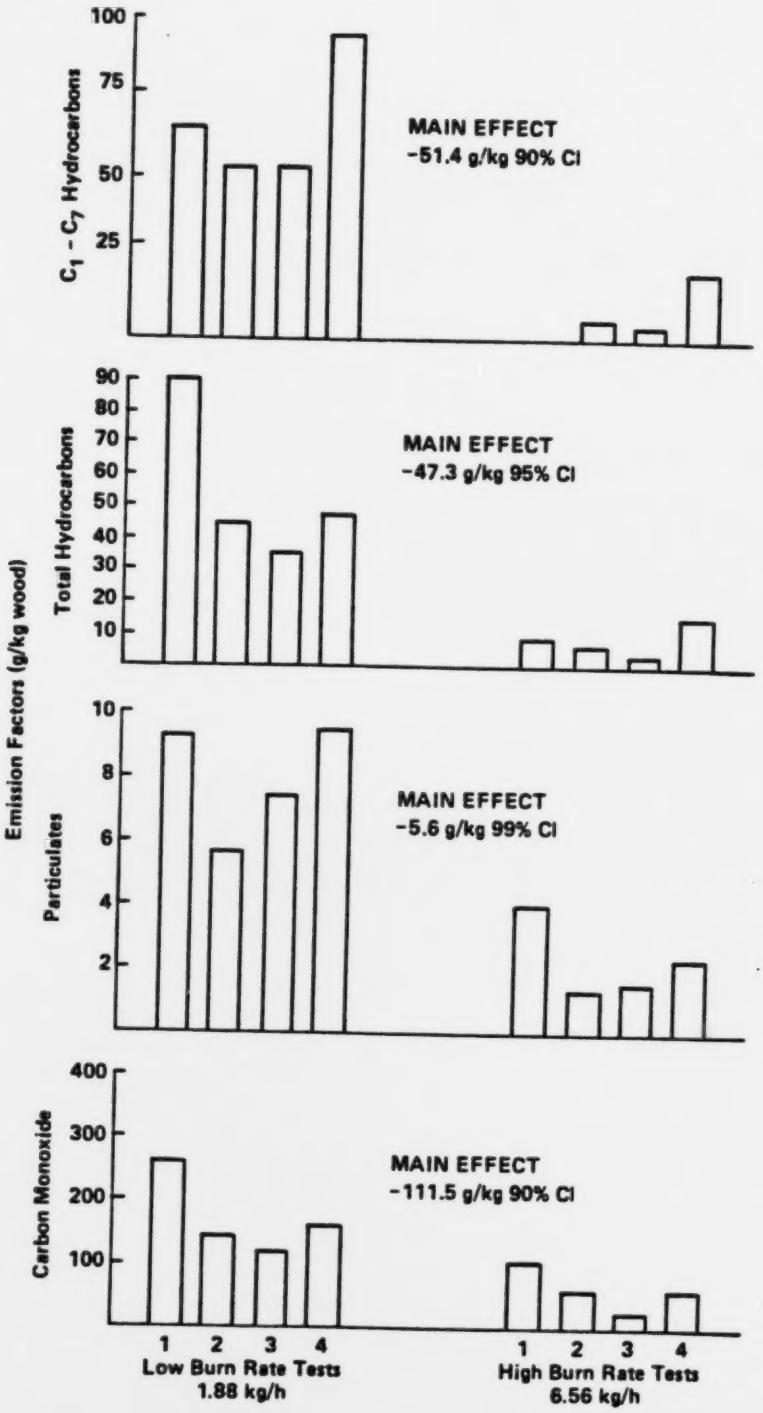


**Figure 2.** The effect of low and high burn rates on carbon monoxide, particulate, total hydrocarbon, and $C_1$-$C_7$ hydrocarbon emission factors (g/kg wood).

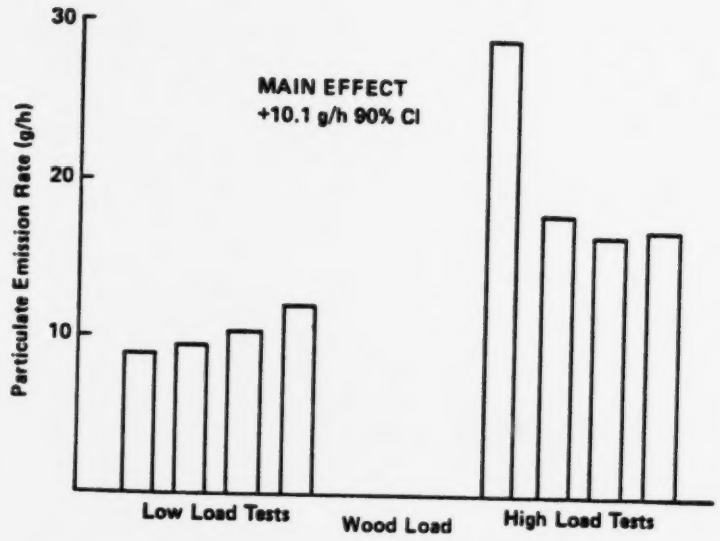


Figure 3. The effect of low and high wood load tests on particulate emission rate (g/hr).

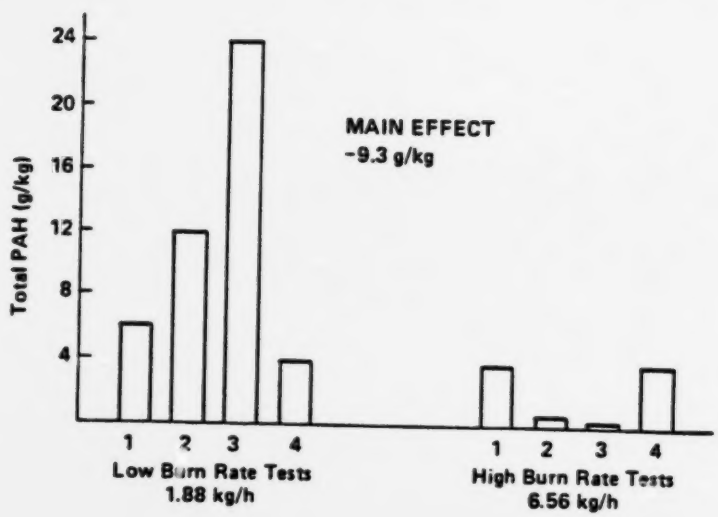


Figure 4. The effect of low and high burn rates on total PAH emissions factors (g/kg wood).

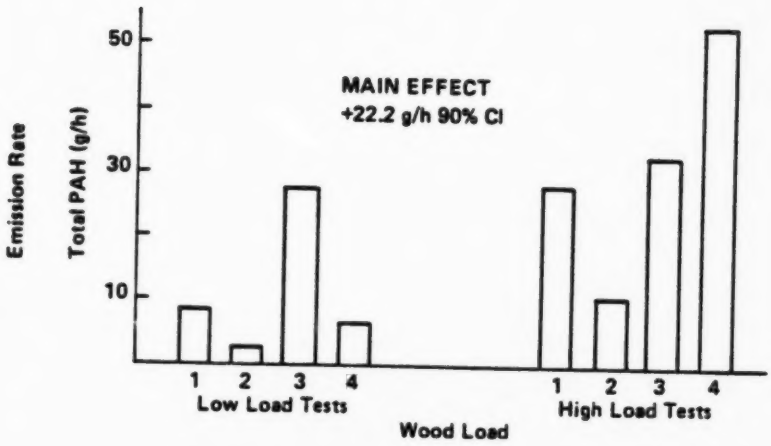


Figure 5. The effect of low and high wood load tests on total PAH emission rate (g/hr).

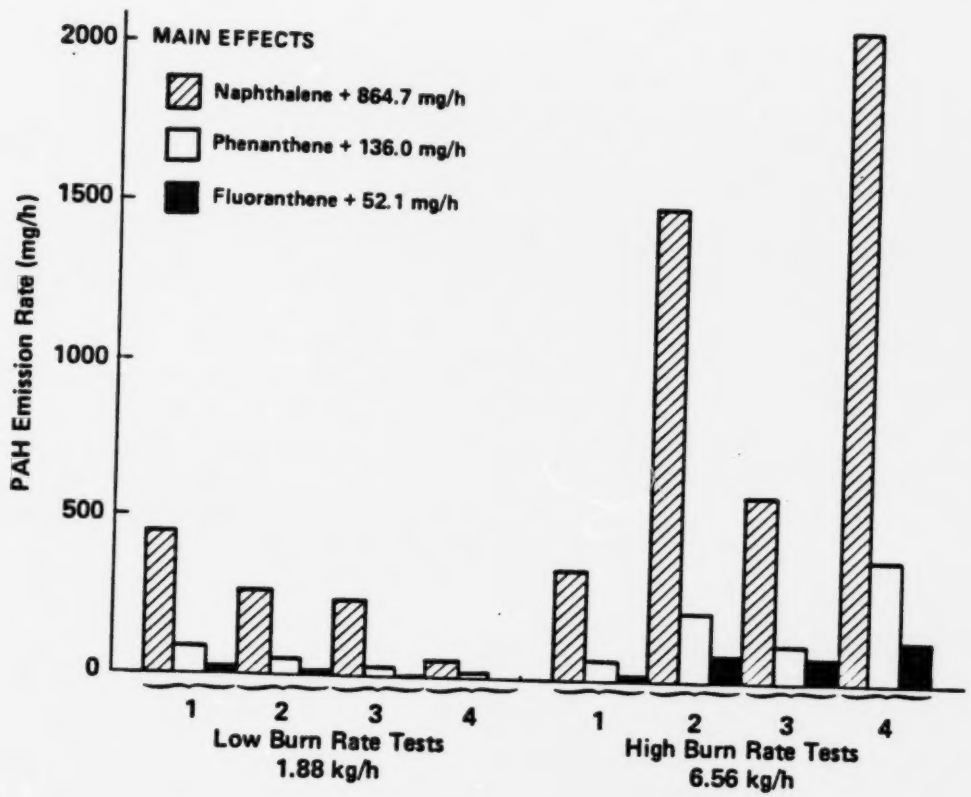


Figure 6. The effect of low and high burn rate tests on naphthalene, phenanthrene, and fluoranthene emission rates (mg/hr).

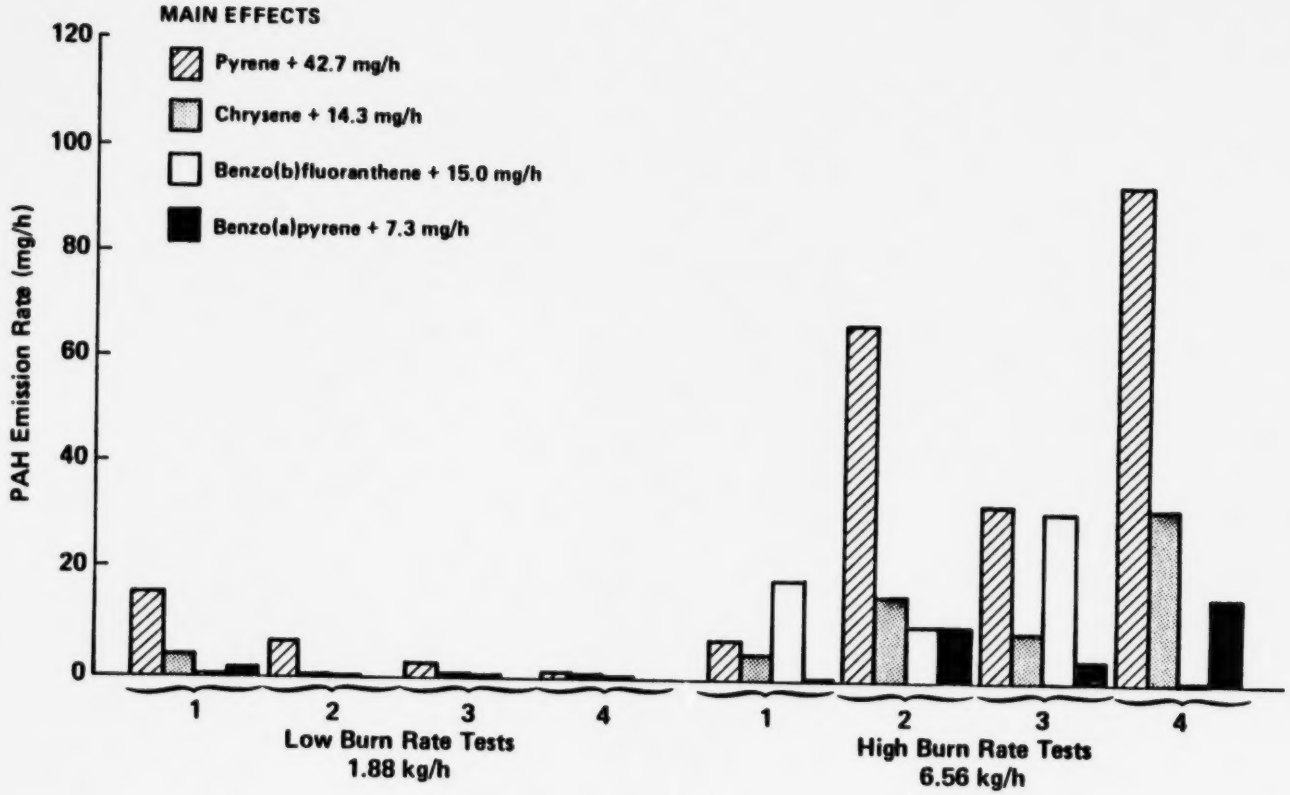


Figure 7. The effect of low and high burn rates on pyrene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene emission rates (mg/hr).

TABLE I. HALF-FACTORIAL TEST MATRIX USED IN THE EXPERIMENTAL TEST DESIGN

| TEST NO. | MEASURED VALUE | VARIABLES FUEL | MOISTURE | LOAD | BURN RATE |
|---|---|---|---|---|---|
| 1 | V1 | + | + | + | + |
| 2 | V2 | + | + | - | - |
| 3 | V3 | + | - | + | - |
| 4 | V4 | + | - | - | + |
| 5 | V5 | - | + | + | - |
| 6 | V6 | - | + | - | + |
| 7 | V7 | - | - | + | + |
| 8 | V8 | - | - | - | - |

| | RUN 1 | RUN 2 | RUN 3 | RUN 4 | RUN 5 | RUN 6 | RUN 7 | RUN 8 | RUN 9 REP 3 | RUN 10 DUP 2 | AVE | %DIFF |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RTI RUN No. | 50403 | 50411 | 50417 | 50424 | 50501 | 50508 | 50515 | 50522 | 50605 | 50612 | R2R10 | R2R10 |
| FUEL | OAK | OAK | OAK | OAK | PINE | PINE | PINE | PINE | OAK | OAK | OAK | |
| MOISTURE | CURED | CURED | UNCURED | UNCURED | CURED | CURED | UNCURED | UNCURED | UNCURED | CURED | CURED | |
| (grav %) | 18.7 | 18.7 | 34.9 | 34.9 | 15.1 | 15.1 | 31.6 | 31.6 | 34.9 | 18.7 | 18.7 | 0.0 |
| LOAD | HIGH | LOW | HIGH | LOW | HIGH | LOW | HIGH | LOW | HIGH | LOW | LOW | |
| (initial kg) | 17.00 | 8.00 | 20.30 | 12.60 | 12.00 | 6.40 | 13.80 | 5.40 | 13.00 | 7.00 | 7.90 | 22.8 |
| BURN RATE | HIGH | LOW | LOW | HIGH | LOW | HIGH | HIGH | LOW | LOW | LOW | LOW | |
| (m5 kg/hr) | 7.20 | 1.25 | 3.53 | 6.83 | 1.87 | 5.31 | 6.92 | 2.17 | 2.22 | 1.24 | 1.25 | 0.9 |

TABLE II. STATISTICALLY SIGNIFICANT RESULTS WITH A MEASURE OF THE MAIN EFFECT FROM EACH PARAMETER

| TEST PARAMETER | BURN RATE | | WOOD MOISTURE | | WOOD LOAD | | WOOD TYPE | |
|---|---|---|---|---|---|---|---|---|
| FROM TO | 1.88 → 6.56 kg/hr | | 33.2 → 16.9 % | | 8.3 → 1.40 kg | | Pine→Oak | |
| | CI[1] | ME | CI | ME | CI | ME | CI | ME |
| Stack Flow ($m^3$/min) | 99% | +0.70 | 95% | +0.29 | 90% | +0.22 | | |
| Stack Moisture (%) | | | 95% | -5.17 | | | | |
| Stack Temperature (°C) | 99% | +170.1 | | | | | | |
| Stove Temperature (°C) | 99% | +143.8 | | | | | | |
| Particulates ($g/m^3$) | 95% | -0.27 | | -0.035 | | +0.093 | | |
| (g/hr) | | | | | 90% | +10.06 | | |
| (g/kg) | 99% | -5.63 | 90% | +2.22 | | +1.54 | | |
| TOTAL PAH (PAH GRAV + PAH TCO) | | | | | | | | |
| TOTAL PAH ($g/m^3$) | | -0.64 | | -0.73 | | | | |
| (g/hr) | | | | -19.36 | 90% | +22.22 | | |
| (g/kg wet wood) | | -9.3 | | -7.25 | | | | |
| NAPHTHALENE ($mg/m^3$) | | | 90% | -14.20 | | | | |
| (mg/hr) | | +864.67 | | -670.5 | | | | |
| ACENAPHTHYLENE ($mg/m^3$) | | | | -1.95 | | | | |
| (mg/kg wet wood) | | | | | | | | -24.5 |
| FLUORENE ($mg/m^3$) | | | | -0.64 | | | | -0.55 |
| (mg/kg wet wood) | | | | | | | | -9.46 |
| PHENANTHRANE ($mg/m^3$) | | | | | | | | -4.51 |
| (mg/hr) | | +136.0 | | | | | | |
| (mg/kg wet wood) | | | | | | | | -22.92 |
| ANTHRACENE ($mg/m^3$) | | | | -0.37 | | | | |
| (mg/kg wet wood) | | | | | | | | -4.51 |
| PYRENE ($mg/m^3$) | | +0.58 | | | | | | |
| (mg/hr) | | +42.7 | | | | | | |

(1)Where there are no confidence intervals (CI) shown with the main effect, the f-values generated for that main effect (ME) fell just below the requirement for a 90% confidence interval. Those main effects were reported since the f-values were still much higher than the values observed when there was clearly no significance.

TABLE III. STATISTICALLY SIGNIFICANT RESULTS WITH A MEASURE OF THE MAIN EFFECT FROM EACH PARAMETER

| TEST PARAMETER | BURN RATE | | WOOD MOISTURE | | WOOD LOAD | | WOOD TYPE | |
|---|---|---|---|---|---|---|---|---|
| FROM TO | 1.88 → 6.56 kg/hr | | 33.2 → 16.9 % | | 8.3 → 1.40 kg | | Pine→Oak | |
| | CI[1] | ME | CI | ME | CI | ME | CI | ME |
| Cadmium ($\mu g/m^3$) | | | 90% | -4.88 | | | | |
| (mg/hr) | | +0.207 | | | | -.106 | | |
| (mg/kg wet wood) | | | 90% | -0.04 | | | | |
| Potassium ($\mu g/m^3$) | 90% | +1541.9 | | | | | 95% | +1852.9 |
| (mg/hr) | 95% | +135.5 | | | | | 90% | +97.89 |
| (mg/kg wet wood) | 95% | +11.77 | | | | | 99% | +20.02 |
| Manganese ($\mu g/m^3$) | 90% | +8.98 | | | | | 95% | -16.02 |
| (mg/hr) | 90% | +1.01 | | | | | 90% | -1.02 |
| (mg/kg wet wood) | | | | | | | 95% | -0.27 |
| Sulfur ($\mu g/m^3$) | 90% | +867.44 | | | | | | |
| (mg/hr) | 95% | +64.68 | | | | | | |
| (mg/kg wet wood) | 95% | +7.52 | | | | | | +5.25 |
| Zinc ($\mu g/m^3$) | 90% | +158.84 | | | | | | -136.44 |
| (mg/hr) | | +11.64 | | | | | | |
| (mg/kg wet wood) | | | | | | | 90% | -2.05 |

[1]Where there are no confidence intervals (CI) shown with the main effect, the f-values generated for that main effect (ME) fell just below the requirement for a 90% confidence interval. Those main effects were reported since the f-values were still much higher than the values observed when there was clearly no significance.